Inorganica Chimica Acta, 39 (1980) 249–255
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Nickel(II), Palladium(II) and Cobalt(II) Complexes of the Substituted Tritertiary Arsine, 2-Chloroethylbis(3-dimethylarsinopropyl)arsine

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Received September 3, 1979

The substituted tritertiary arsine, 2-chloroethylbis(3-dimethylarsinopropyl)arsine, forms $Ni(trias)X_2$ *(X = Cl, Br, I), which are assigned tetragonal pyramidal pentacoordinate structures. The* $Pd(trias)Cl_2$ *species is best assigned as a planar* $[Pd(trias)Cl]Cl$ *coordination moiety. Both* $[Co(trias)Br]_2[CoBr_4]$ *and* $[Co(trias)Br]ClO_4$ *contain pseudotetrahedral cations, but* $[Co(trias)_2](ClO_4)_2$ *is unlike any four-coordinate or six-coordinate cobalt(II) entity and is assigned a pentacoordinate structure containing a tridentate and a bidentate ligand. The donor properties of trias are compared to that of similar tridentate ligands.*

Introduction

The coordination chemistry involving potentially tridentate phosphines, arsines or phosphine–arsine ligands has provided some quite fascinating insights into the relative role which metal and ligand, electronic and steric factors play in determining the stoichiometry and structure of the resulting complex.

The flexible ligands with trimethylene backbones, $RE(CH_2CH_2CH_2AsMe_2)_2$ (RE = PhP [2], MeAs [2], PhAs [3]) forms five-coordinate square pyramidal $[NiLX_2]$ (X = Cl, Br, I for all ligands, X = NCS, CN when RE ≠ PhAs), which remain predominantly pentacoordinate in solution; the nickel(II) perchlorate complexes are all of the type $[Ni_2L_3(H_2O)](ClO_4)_4$ [2, 3]. Four coordinate $[Ni\{PhP(CH_2CH_2CH_2AsMe_2)_2\}Cl]ClO_4$ is formed by reaction of the ligand with '$NiClClO_4$', or on boiling $[Ni_2L_3(H_2O)](ClO_4)_4$ in methanol [2] during which the ligand reduces ClO_4^- to Cl^-. With $PhAs(CH_2CH_2CH_2AsMe_2)$ a number of discrete cations, viz. $[Ni_3L_5]^{6+}$, $[NiL_2]^{2+}$, $[Ni_2L_3I_3]^+$ and $[Ni_4L_4I_7]^+$ can be isolated [3]. The more rigid $MeAs(o\text{-}C_6H_4AsMe_2)_2$ forms five-coordinate $[NiLX_2]$ (X = Br, I) and $[NiL_2][Ni(NCS)_4]$ ($NiAs_5$ donor set), and there is also a paramagnetic $NiLCl_2$ of unknown structure [4].

Very few complexes of cobalt(II) containing these ligands have been obtained. The very 'soft' $PhAs(o\text{-}C_6H_4AsPh_2)$ does not complex, but $PhP(o\text{-}C_6H_4AsPh_2)_2$ forms pentacoordinate $[CoLX_2]$ (X = Br, NCS) [5], contrasting with the isolation of octahedral $[Co(ttas)_2]^{2+}$ (ttas = $MeAs(o\text{-}C_6H_4AsMe_2)_2$) [6].

Complexes $[Pd(TAS)X_2]$ (TAS = $PhAs(o\text{-}C_6H_4AsPh_2)_2$) have been assigned a distorted trigonal bipyramidal structure [7]; the methyl-substituted analogue $MeAs(o\text{-}C_6H_4AsMe_2)_2$ forms [MLX]X which are planar and 1:1 electrolytes for M = Pt, but the palladium(II) complexes exhibit non-electrolyte behaviour in acetone and are presumably pentacoordinate in this solvent [4].

We have recently embarked on the synthesis of ligands of type $(H_2C{=}CHCH_2CH_2)_nAs(CH_2CH_2CH_2AsMe_2)_{3-n}$ and a study of their donor properties [8, 9]. The organoarsenic chemistry involved in preparing some of these ligands is quite intricate. One crucial intermediate is 2-chloroethylbis(3-dimethylarsino)arsine, trias, the preparation of which is outlined in Scheme I. We have been able to isolate and characterise divalent nickel, palladium and cobalt complexes of this ligand, which we report here. Thus, as well as extending the knowledge of triarsine derivatives of nickel(II), this study has expanded on the paucity of information available on palladium and cobalt analogues. We compare trias with the donor properties of $MeAS(CH_2CH_2CH_2AsMe_2)_2$ (tas) and $PhAs(CH_2CH_2CH_2ASMe_2)_2$ (tasp).

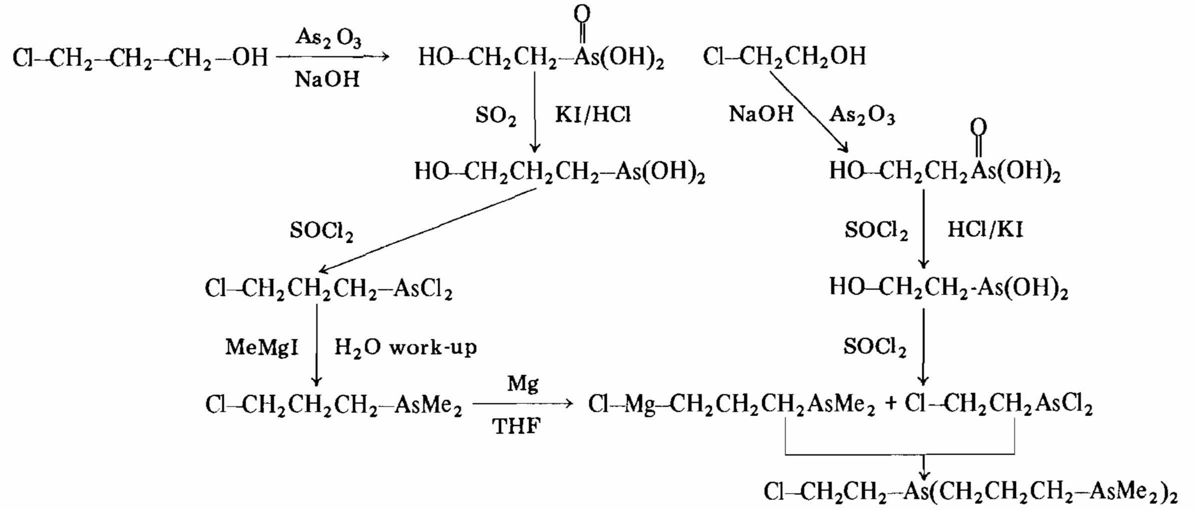
Results and Discussion

Addition of trias to an ethanolic solution of NiX_2 (X = Cl or Br) under nitrogen gave an intense

TABLE I. Analytical and Some Physical Data of the Complexes of trias.

Complex	Colour	M.Pt.[a]	% Calc.			% Found			M[b]	μ_{eff}[e]
			C	H	Hal	C	H	Hal		
$Ni(trias)Cl_2$	deep purple	215	25.7	5.0	19.0	22.7	4.4	24.1	52 (c)	
$Ni(trias)Br_2$	deep purple	250	22.0	4.3	24.6	22.0	4.2	24.5	30 (b)	0.2
$Ni(trias)I_2$	green-black	250	19.4	3.8	33.8	19.1	3.6	33.9	18 (c)	
$Pd(trias)Cl_2$	yellow	184	23.6	4.6	11.7	22.7	4.5	11.5	48 (c)	
$[Co(trias)Br]_2[CoBr_4]$	green	250	18.9	3.7		18.7	3.8		110 (d)	4.26
$[Co(trias)Br]ClO_4$	green	215	21.4	4.3		21.7	4.5		135 (d)	4.28
$[Co(trias)_2](ClO_4)_2$	dark purple	145	25.7	5.1		26.1	5.6		155 (c)	2.25

[a] Melting point or decomposition point. [b] Molar conductance, $cm^2\ ohm^{-1}\ mol^{-1}$. [c] 10^{-3} molar solution in nitromethane. [d] 3×10^{-4} molar solution in DMF. [e] Measured at 27 °C (300 K), Bohr Magnetons; the moment recorded is that of the cationic species.



Scheme I

trias

purple colour. Concentration of the solution and cooling in ice precipitated deep red-purple crystals of empirical formula $Ni(trias)X_2$ (X = Cl or Br). Recrystallisation of the bromo-complex gave a pure phase, but it proved impossible to isolate a pure chloro-complex. Decomposition of this complex always took place to some extent, and the solid phase isolated from solution always contained some nickel(II) chloride (see Table I). A similar reaction of trias and NiI_2 gave an immediate dark green precipitate; recrystallisation from iso-propanol yielded dark green, almost black, crystals of the analogous $Ni(trias)I_2$ complex (Table I).

The chloro- and bromo- complexes are readily soluble in most polar solvents, but the iodo-complex is only sparingly soluble in organic solvents. The conductance of the $Ni(trias)X_2$ complexes in nitromethane indicate some dissociation in solution, Table I. The chloro-complex exhibits a value (52 $cm^2/ohm^{-1}\ mol^{-1}$) not far removed from that expected of a 1:1 conductor (70–90 $cm^2\ ohm^{-1}\ mol^{-1}$), and is probably a result of extensive dissociation to give a $[Ni(trias)Cl]Cl$ species. The difficulty in isolating a pure $Ni(trias)Cl_2$ phase may well result from the low stability of the pentacoordinate species with respect to dissociation in solution. It might be noted that no chloro-complex could be isolated with tas [10] although a pure $NiLCl_2$ phase was isolated when L = tasp[3]. The conductances of the bromo- and iodo-complexes are much nearer to those expected for a non-electrolyte (30 and 18 $cm^2\ ohm^{-1}\ mol^{-1}$). Barclay, Nyholm and Parish [10] have suggested that a pentacoordinate $[NiLX_2]$ complex increases in stability as the polarisability of X increases, and the results with trias confirm that the stability of the $[Ni(trias)X_2]$ species decreases as I > Br > Cl. McAuliffe and Levason [11] have noted that arsine complexes are sometimes difficult to form and isolate

TABLE II. Electronic spectral Data for the Ni(II) Complexes of trias.

Compound	E_{max} solution[a] kK	(ϵ_{max})	E_{max} solid state kK
Ni(trias)Cl$_2$			6.1
	12.8	(150)	14.0
	21.0	(745)	20.1
	26.7	(550)	26.7
Ni(trias)Br$_2$			5.9
	12.2	(250)	13.6
	about 18.8	sho	
	20.7	(800)	19.4
	26.2	(2200)	27.6
Ni(trias)I$_2$			5.4
	11.9	(830)	12.4
	15.7	(1130)	16.4
	19.0	(870)	
	24.1	(2400)	23.5
			26.7
	31.9	(15.300)	
	35.6	(14.450)	

[a] In nitromethane solution.

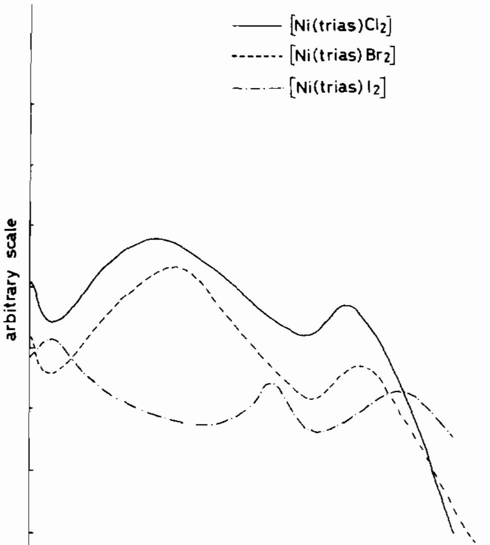


Fig. 1. Reflectance spectra of the Ni(trias)X$_2$ complexes.

in alcoholic media when the donor set is particularly soft; nickel(II) occupied a borderline position between hard and soft acids, and the hard alcoholic oxygen donor atoms compete with the arsine for co-ordination.

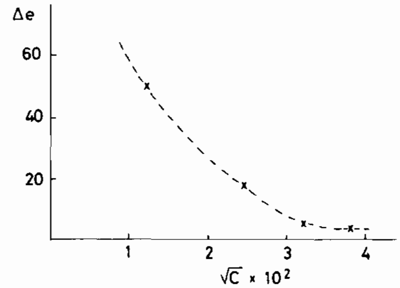


Fig. 2. Conductivity–dilution studies of the Pd(trias)Cl$_2$ complex.

The electronic spectra of the Ni(trias)X$_2$ complexes are reported in Table II and Fig. 1. The solution spectra were obtained in nitromethane between 26 kK and 12 kK, and the broad intense absorption at 19–21 kK is consistent with a tetragonal pyramidal structure for the Ni(trias)X$_2$ series. The spectra closely resemble that of Ni(tas)Br$_2$, which is known to have a pentacoordinate distorted tetragonal pyramidal structure [12]. There is also excellent agreement with the electronic spectra reported for Ni(tasp)X$_2$ [3]. There is a certain amount of asymmetry about the absorption bands in the 21–18 kK region of the spectra of the bromo- and iodo- complexes, Table II, and this is presumably due to the distortion from a regular tetragonal pyramidal structure needed to accommodate the larger halide ions. The reflectance spectra obtained between 30 kK and 4 kK are in overall agreement with the solution spectra. The differences in band position and profile, Fig. 1, indicate some slight change in structure in the solid and solution states; this small discrepancy has been noted in the Ni(tasp)X$_2$ series [3]. The normal spectrochemical series is observed in the Ni(trias)X$_2$ complexes *i.e.* Cl > Br > I.

The addition of trias to an ethanolic solution of Na$_2$PdCl$_4$ under nitrogen gave a pale yellow solution which yielded a bright yellow crystalline solid of empirical formula Pd(trias)Cl$_2$, Table I. The yellow complex is very soluble in polar organic solvents, and conductivity measurements in nitromethane and 1,2-dichloroethane gave values intermediate between those expected for a non-electrolyte and a 1:1 conductor, Table I. Conductivity-dilution studies of Pd(trias)Cl$_2$ in nitromethane were obtained, and a plot of Δ_m against $\sqrt{c}$ is recorded in Fig.2. The conductance increases very rapidly at concentrations below 5×10^{-4} molar. The data is best interpreted as a dissociation in solution to give four-coordinate [Pd(trias)Cl]Cl species; at low concentrations this dissociation becomes much more extensive and eventually the conductance reaches a value indicative of complete dissociation. The analogous Pd(tas)Cl$_2$ exhibits similar behaviour in solution [10].

TABLE III. Electronic Spectral Data of the Co(II) and Pd(II) Complexes of trias.

Complex	Solution		Solid
	E_{max} kK	(ϵ_{max})	E_{max} kK
Pd(trias)Cl_2	28.8	(1420)[a]	about 26.7 sh
	37.5 sh	(8500)	
	41.9	(16.100)	
[Co(trias)Br]$_2$[$CoBr_4$]	6.0	[a]	5.9
			13.5 sh
	14.8		14.5
	15.5		15.4
	about 16.0 sh		16.5 sh
[Co(trias)Br]ClO_4	not recorded		7.1
			15.2
			15.6
			about 27.0 sh
[Co(trias)$_2$](ClO_4)$_2$		[a]	5.9
			7.7
	13.0	(100)	about 14.5 sh
	22.5	(1650)	20.0

[a] In nitromethane. [b] In DMF.

The electronic spectrum of Pd(trias)Cl_2 was obtained in nitromethane and 1,2-dichloroethane solution, Table III. The absence of absorption bands in the 20–25 kK region precludes a pentacoordinate structure in solution. The reflectance spectrum of the solid complex is similarly free from absorption in this region. The only absorption below 30 kK in both solid and solution is a shoulder on the tail of a charge transfer band. The most probable interpretation of these results are that in solution the complex has a four co-ordinate [Pd(trias)Cl] Cl structure; in concentrations of about 10^{-3} *M* or greater some association takes place. In the solid state, the structure is intermediate between TP and square planar; an ill-defined shoulder in the 22 kK region is present in the reflectance spectrum.

The cobalt(II) complexes of trias proved rather more difficult to isolate than the nickel species. The addition of trias to $CoCl_2$ in ethanol or dichloromethane gave green solutions which quickly turned brown. Removal of the solvents gave sticky green oils which were very hygroscopic and defied all attempts to crystallisation. The addition of ClO_4^- or BPh_4^- ions to ethanolic solutions of the oils failed to give an isolatable solid phase.

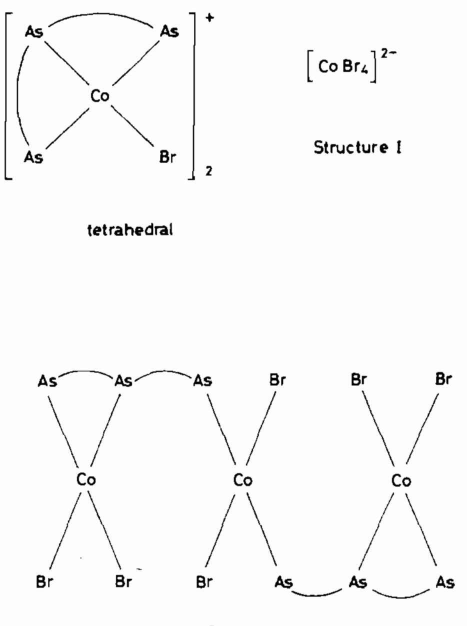


Fig. 3. Two possible configurations for the cobalt complex of trias.

Under similar conditions, trias and $CoBr_2$ gave a brown solution which quickly began to precipitate a bright green solid. Repeated washing with hot ethanol and dichloromethane yielded a green solid of empirical formula $Co_3(trias)_2Br_6$, Table I. Evaporation of the mother liquor gave dark green-brown oils which could not be crystallised. The green complex proved to be virtually insoluble in all common solvents. Refluxing the solid as a suspension in ethanol

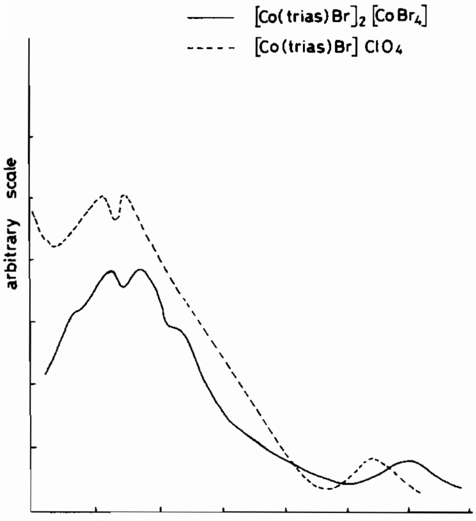


Fig. 4. Electronic spectra of the Co(II)–tasol complexes (reflectance).

with $NaClO_4$ or $NaBPh_4$ gave identical green solids which proved to slightly impure $Co_3(trias)_2Br_6$.

Two possible structures for the $Co_3(trias)_2Br_6$ complex are given in Fig. 3. Either structure would account for the low solubility in polar organic solvents. The green complex is slightly soluble in N,N-dimethylformamide and a solution (about 3×10^{-4} molar) in DMF exhibits a conductance of 110 cm^2 ohm^{-1} mol^{-1}. The accepted range of conductance values for a 2:1 electrolyte in DMF is 130–170 cm^2 ohm^{-1} mol^{-1} (these values refer to 10^{-3} molar solutions); however for complexes containing large ions such as BPh_4^- values can be as low as 115 cm^2 ohm^{-1} mol^{-1} [13]. A conductance value of 110 is reasonable for a complex (Structure I) with the large $Co(trias)Br^+$ and $CoBr_4^{2-}$ ions.

The mull infrared spectrum of the $Co_3(trias)_2Br_6$ complex provides further evidence for an ionic structure I. The spectrum exhibits a strong broad absorption at around 225 cm^{-1}; Sabatini and Sacconi have proposed that a strong band at 225–230 cm^{-1} region is diagnostic of the presence of the $CoBr_4^{2-}$ ion [14]. A medium band at 270 cm^{-1} is in the correct region for ν(Co–Br) in a tetrahedral cobalt(II) complex [15]. Thus, the infrared spectrum is consistent with the formulation of the green complex as structure I *i.e.* a tetrahedral $[Co(trias)Br]_2[CoBr_4]$ species.

The reflectance spectrum of the green complex provides further evidence for this (Fig. 4 and Table III). The spectrum exhibits a weaker absorption band at 6.0 kK and a stronger group of absorptions in the 16–13 kK region. There are at least four bands under the profile – 16.5, 15.4, 14.5 and 13.5 kK, respectively. The last two bands are assigned to the spectrum of the $[CoBr_4]^{2-}$ ion; the spectrum of this ion has been shown to consist of two strong bands at about 14.2 and 13.4 kK (ϵ is about 1000) and two weaker bands at about 15.0 and 15.6 kK (ϵ is about 200). The strong absorption at 16.5 and 15.4 kK are assigned to the $Co(trias)Br^+$ ion, and mask the weaker absorptions of the $CoBr_4^{2-}$ ion.

The magnetic susceptibility of the $[Co(trias)Br]_2$-$CoBr_4$ species was measured at 300 K. By subtracting 10640×10^{-6} c.g.s. units attributable to the $[CoBr_4]^{2-}$ ion, from the total molar susceptibility, a magnetic moment of 4.26 B.M. is found for the $[Co(trias)Br]^+$ cation. Pseudotetrahedral Co(II) complexes have typical magnetic moments of 4.2 to 4.4 B.M. when the complexes contain arsines and phosphines [16], and the magnetic data is in excellent agreement with our assignment.

Further evidence for the formation of a $[Co(trias)Br]^+$ cation is provided by isolation of a $[Co(trias)Br]ClO_4$ complex. Although it proved impossible to exchange the $CoBr_4^{2-}$ ion once the complex has formed, addition of trias to a solution of '$CoBrClO_4$' gave an immediate precipitate of the olive green $[Co(trias)Br]ClO_4$ complex (Table I). This species is virtually insoluble in all common solvents except DMF; solutions in this solvent are very unstable but the conductance of a fresh solution is consistent with the complex being a 1:1 electrolyte in DMF, Table I. A room temperature magnetic moment of 4.28 B.M. is in good agreement with the previous assignment of the $[Co(trias)Br]^+$ cation.

The mull infrared spectrum of the $[Co(trias)Br](ClO_4)$ complex is consistent with the empirical formulation. The band at 270 cm^{-1}, ν(Co–Br), is present in the spectrum, but the band at 225 cm^{-1} (ν(Co–Br) for the $CoBr_4^{2-}$ anion) is absent. A strong broad unsplit absorption band at 1085 cm^{-1} is indicative of the presence of ionic perchlorate ion [17].

The electronic reflectance spectrum was recorded between 30 kK and 5 kK (see Table III and Fig. 4). The absorption bands assigned to the $CoBr_4^{2-}$ anion are absent, and the spectrum profile is consistent with a pseudotetrahedral $[Co(trias)Br]^+$ cation [18].

It is interesting to compare the behaviour of trias with other tridentate arsines with respect to their behaviour with Co(II). The reaction of CoX_2 (X = Br, I or NCS) with tasp, $PhAs(CH_2–CH_2–CH_2–AsMe_2)_2$, gave a mixture of products; the main product was $[Co(tasp)X]_2[CoX_4]$ but it proved possible to isolate the pentacoordinate $[Co(tasp)X_2]$ species in small yield [19]. The ligand ttas, $MeAs(o\text{-}C_6H_4\text{-}AsMe_2)_2$, was reported to show very different behaviour [6]. It proved very difficult to isolate Co(II)–ttas complexes of any kind; unstable $[Co(ttas)_2][CoCl_4]$ and $[Co(ttas)_2][ClO_4]_2$ complexes were isolated but proved very easily oxidised to Co(III) species. A series of $[CoLX_3]$ complexes

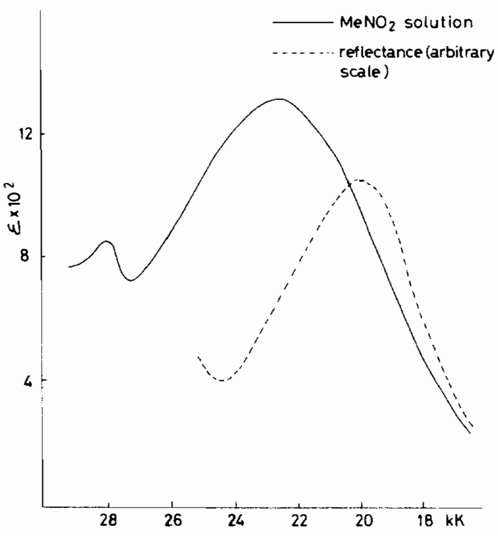


Fig. 5. Electronic spectra of the $Co(trias)_2(ClO_4)_2$ complex.

were reported however [6]. It is difficult to deduce an obvious trend in this behaviour; the situation is complicated by the non-equivalence of the ligand geometries. If the softness of the donor set is taken to decrease at ttas > trias ~ tasp, then the tendency to pentacoordination follows a similar pattern. However, it is difficult to reconcile the fact that the hybrid $PhP(o\text{-}C_6H_4AsPh_2)_2$ with a harder donor set than ttas gives stable pentacoordinate $[CoLX_2]$ species as the only product [5].

It must be stressed that while no quantitative investigations were made, the Co(II) trias complexes are indefinitely stable in air at room temperature. The reaction of trias with $Co(ClO_4)_2$ was investigated to compare the behaviour of trias and ttas. The addition of trias to an ethanolic solution of $Co(ClO_4)_2$ gave an immediate precipitate of a dark purple solid. Analytical data established an empirical formula of $Co(trias)_2(ClO_4)_2$ for the complex. Although it is slightly hygroscopic, the species is indefinitely stable in air.

The purple complex is easily soluble in polar organic solvents; conductance of a 10^{-3} solution in nitromethane is in the range expected for a 2:1 electrolyte (see Table I). A plot of $\Delta_o - \Delta_m$ against $\sqrt{C}$ gives a slope of 425, again in accord with a 2:1 electrolyte [20]. The mull infrared spectrum exhibits absorption bands at 1095 cm^{-1} (very strong and broad) and 625 cm^{-1} (strong and sharp), indicative of the presence of ionic perchlorate groups [17].

The electronic spectra of the species are reported in Table III and Fig. 5. The spectral profile is very different to that of a four-coordinate Co(II) complex, nor is it similar to that of an octahedral complex. The most reasonable assignment is that of a pentacoordinate complex; low spin pentacoordinate Co(II) is usually diagnosed by the presence of an absorption band in the 20 to 23 kK region [21]. The absorption band is very broad for a complex with this structure, and there is some considerable difference in E_{max} for solid and solution studies. However, a similar pentacoordinate structure is assigned in the solid and solution state. The spectra reported for the $[Co(ttas)X_3]$ species are quite different, the main absorption being at about 17 kK, with a shoulder at about 25 kK [6]. Unfortunately, the spectra of the $[Co(ttas)_2]^{2+}$ cations were not reported; they were assigned a low-spin penta-coordinate structure on the basis of magnetic measurements [6].

The room temperature magnetic moment of the $[Co(trias)_2](ClO_4)_2$ complex is 2.25 B.M.; low-spin pentacoordinate Co(II) complexes have magnetic moments between the ranges for low-spin octahedral (μ = 1.8 to 2.0 BM) planar (μ = 2.3 to 2.9 BM) complexes.

Thus all the available evidence indicates a low spin pentacoordinate structure for this species. The solubility of the complex, and the conductivity-dilution studies, preclude a polynuclear species. Presumably, pentacoordination is achieved by one tridentate and one bidentate ligand; this type of behaviour is well known for Ni(II)–triarsine complexes [22]. Attempts to verify the presence of an uncoordinated arsine group by the change in conductivity of the complex in solution upon the addition of methyl iodide* proved unsuccessful, since addition of methyl iodide caused immediate decomposition of the solution.

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*The addition of methyl iodide should quaternarise the free $-AsMe_2$ group to give a $-AsMe_3^+I^-$ group. The conductivity of the solution should increase accordingly.

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